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Description

The present invention relates to a catalyst which hydrotreats hydrocarbons without need to be activated.

In the hydrotreating process, hydrocarbon oils are hydrogenated, desulfurized, denitrified, cracked, or otherwise treated under the presence of hydrogen. For such a process, a catalyst is used in a carrier made from an inorganic oxide, such as alumina, silica alumina, or titania. The catalyst contains at least one kind of metal selected from the Groups VI and VIII of the Periodic Table to promote hydrotreating. M_o and W are frequently used as Group VI metals. C_o and N_i are often employed as Group VIII metals.

Usually, these metals are contained in the form of oxides. Since they are not active as they are, it is necessary to transform the oxides into sulfides to activate them before they are subjected to a hydrotreating process, i.e., presulfiding is necessitated.

Generally, the presulfiding is effected by passing a sulfurizing agent through a catalyst bed together with hydrogen after the catalyst is loaded into a reactor in which hydrocarbon oil is hydrotreated. The operating conditions of the preliminary sulfurization differ depending on the hydrotreating process and also on the used sulfurizing agent. Where hydrogen sulfide is used, about 0.5 to 5% by volume of hydrogen sulfide is contained in hydrogen, and 1000 to 3000 l (at normal temperature and normal pressure) of this compound is employed per liter of the catalyst. The temperature is in excess of 180°C. Normally, the temperature is higher than 250°C. Where carbon disulfide, normal butyl mercaptan, dimethyl sulfide, dimethyl disulfide, or other similar material is utilized, it is diluted with a light hydrocarbon oil. The conditions are as follows. Temperature is 250 to 350°C. The pressure is 20 to 100 Kg/cm². The liquid space velocity is 0.5 to 2 hr⁻¹. The ratio of hydrogen to oil is 200 to 1000 Nl/l. After the presulfiding process is carried out in this way, the feedstock to be treated is introduced, and the hydrotreating process is initiated.

The aforementioned presulfiding process determines whether the subsequent hydrotreating process succeeds and, therefore, appropriate selection of the used materials and careful operations are needed. As an example, when a diluting agent is used, if it contains olefins, then the resulting polymers poisons the catalyst. For this reason, it is necessary to employ a hydrocarbon oil containing no olefins. Where the viscosity is high, the wettability on the surface of the catalyst is low and so heavy oils are inappropriate. Consequently, the use of light distillates is forced. This results in an increase in the cost. If a metal catalyst reacts with hydrogen at a high temperature and is reduced, then it is passivated. To prevent this undesirable phenomenon, a large amount of sulfurizing agent must be used. Also, the ratio of hydrogen to the sulfurizing agent must be maintained at appropriate values. Usually, the presulfiding of this kind is carried out for several days. Because this operation is temporary, it is rarely automated. Thus, unusual complex operations are required. This imposes great burden to the operator. Hence, the omission of the presulfiding or at least a decrease in the complexity of the operations has been required.

It is an object of the present invention to provide a novel catalyst which hydrotreats hydrocarbons without requiring the aforementioned presulfiding.

The above object is achieved in accordance with the teachings of the invention by a catalyst comprising a carrier of an inorganic oxide, the carrier containing a water-soluble compound of a sulfurizing agent and two metals. The compound can further contain phosphorus. The two metals belong to the Groups VI and VIII, respectively, of the Periodic Table. The carrier has pores in which a precursor of a sulfide is formed. The coordination number of the closest Group VI metal which can be found from the radial distribution function around the Group VI metal is less than 0.25 before the use. The function is determined from the Fourier transform of the extended x-ray fine structure of the precursor.

As is well known in the art, examples of carrier of inorganic oxides include alumina, silica alumina, and titania. Especially, alumina and silica alumina are typical examples.

It is also known that the contained active metal belonging to the Group VI of the Periodic Table is preferably M_o or W or both. The metal belonging to the Group VIII is preferably C_o or N_i or both. Either the Group VI metal or the Group VIII metal is used alone, or their mixture is employed. If necessary, phosphorus is added.

Phosphorus is also a known active substance and useful to the novel catalyst. Phosphoric acid is adequate as an impregnant and can be a water solution independent of the above-described water-soluble compound, for impregnation. Alternatively, the catalyst is impregnated with an impregnant containing the water-soluble compound as well as phosphoric acid. In the latter case, the viscosity of the liquid increases as the phosphoric acid content increases, and it becomes more difficult to impregnate the catalyst with the impregnant. Therefore, in this method, the upper limit of the amount of P₂O₅ contained in the catalyst is approximately 8% by weight.

The carrier is impregnated with any of these water-soluble compounds. In accordance with the invention, a sulfurizing agent is added as an impregnant.

Examples of the sulfurizing agent include mercaptocarboxylic acids, such as mercaptoacetic acid and β -mercaptopropionic acid, their salts, bivalent mercaptans, such as ethane dithiol, and 1,4-butanedithiol, amino-

replaced mercaptans, such as 2-aminoethanethiol and 4-amino thiophenol, thio acids, such as thioacetic acid and thiobenzoic acid, mercaptocarboxylic acid esters, such as mercaptomethyl acetate, mercaptoethylhexyl acetate, and mercaptopropionic methyl. The carrier can be impregnated with water solution of any of these sulfurizing agents. The amount of the contained sulfurizing agent is preferably one to three times the amount of 5 sulfur in equivalent weight, the sulfur being necessary for a metal belonging to the Group VI of the Periodic Table and for a metal belonging to the Group VIII to form sulfides, such as M_6S_2 , WS_2 , C_6S , and NiS , which show high activity in a hydrotreating process. If the contained amount is less than this range, the activity is low. If the amount is in excess of this range, the activity is not increased so much and, therefore, it is uneconomical.

The carrier can be impregnated with the sulfurizing agent either after the carrier is impregnated with the 10 active metal or simultaneously with the latter impregnation.

The carrier is impregnated with an active metal. Alternatively, the carrier is impregnated with an active metal, phosphorus, and a sulfurizing agent as mentioned already. After the impregnated carrier dries, a precursor of a sulfide is formed in the pores. During hydrotreating process, the precursor gradually crystallizes.

The process of the crystallization can be traced by investigating the extended x-ray absorption fine structure. 15 Generally, in an absorption spectrum of a substance absorbing x-rays, the absorption coefficient rises rapidly at wavelengths intrinsic to the elements contained in the substance, and tails off with decreasing wavelength. That is, a group of wedge-shaped absorption bands is formed. The wavelengths at which the absorption coefficient rises are called absorption edges. When such an x-ray absorption spectrum is taken with high resolution, relatively sharp waves are observed near the absorption edges within a range of tens of eV in terms of photon energy. This structure is called x-ray absorption near-edge structure (XANES) and reflects the 20 atomic valences of the atoms absorbing x-rays and the chemical coupling between them. The absorption coefficient slightly varies like ripples at higher energies over a broad range of 100 to 1000 eV. This structure is known as extended x-ray absorption fine structure (EXAFS). Various kinds of information including the distances to neighboring atoms and coordination numbers can be obtained by analyzing the fine structure.

In accordance with the present invention we propose a catalyst for hydrotreating hydrocarbons, the catalyst 25 comprising a carrier of an inorganic oxide, the carrier containing a sulfurizing agent and a water-soluble compound of two metals one of which belongs to the Group VI of the Periodic Table, the other belonging to the Group VIII, the carrier having pores in which a precursor of a sulfide is formed, the coordination number of the closest Group VI metal that is found from the radial distribution function around the Group VI metal calculated 30 by Fourier transform of the extended x-ray absorption fine structure of the precursor being less than 0.25 before use. Even if the precursor is activated within the flow of hydrogen, the number is maintained less than 0.25. For the conventional catalyst, it is impregnated with an active metal and then preliminary baked to oxidize the active metal contained in the catalyst. Before the use of the catalyst, the active metal is presulfided. In this case, the coordination number is about 1.5.

The coordination number of the novel catalyst gradually increases with use and eventually makes little difference 35 with the coordination number of the conventional catalyst. However, the novel catalyst is much superior in activity to the conventional catalyst for the following reason.

For the conventional catalyst, the active metal particles within the pores aggregate by the preliminary baking. What are sulfurized by the presulfiding are only these particles. On the other hand, for the novel catalyst, 40 the precursor of the sulfide is formed in all the pores and gradually crystallizes with use, but aggregation is less likely to occur. Therefore, the larger specific surface is maintained. Hence, the high activity is maintained. This can also be seen from the pore distribution within the catalyst. For the conventional catalyst, it hardly differs from the carrier in pore distribution. The active metal particles aggregate in the pores and are sporadically distributed. For the novel catalyst, the peaks are shifted toward smaller diameters as compared with the distribution 45 of the pores in the carrier. This shows that substances of smaller diameters exist in large quantities within pores.

Principle of Analysis Utilizing EXAFS

The principle of local structure analysis utilizing EXAFS (extended x-ray absorption fine structure) is described 50 in *Analysis*, Japan, 1981, 4, pp. 221-228, and explained below. X-rays are absorbed by the photoelectric effect when an inner-shell electron such as K electron is excited to an unoccupied state. The excited electron waves are scattered by the surrounding atoms. A part of the waves returns to the original atom. The excited and outgoing waves interfere with the returning waves. The amount of transition of excited electrons changes according to the energy of the excited electrons, whereby the absorption spectrum has fine structure.

55 The absorption coefficient μ is given by

$$\mu = \frac{1}{d} \ell_n \frac{I_0}{I} \quad (1)$$

where I_0 the intensity of the incident x-rays, d is the thickness of the sample, and I is the intensity of the trans-

mitted x-rays. The absorption coefficient μ holds for all the atoms constituting the substance. The absorption coefficient μ_k of the K electrons of the atom of interest is given by

$$\mu_k = \mu - \mu_B \quad (2)$$

where μ_B is the absorption coefficient of the other electrons. The coefficient μ_k includes K absorption component of a free atom model not having fine structure, and this component is given by μ_0 . The vibration component X of EXAFS is given by

$$X(k) = \frac{\mu_k - \mu_0}{\mu_0} \quad (3)$$

For K electrons, X (k) is theoretically given by

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$$X(k) = \sum_i \frac{N_i}{kR_j^2} |f_j(\pi)| \sin(2kR_j + \Psi_j + 2\delta_j) \times \exp(-\gamma R_j) \exp(-2k^2\sigma_j^2) \quad (4)$$

where $k (= 2\pi/\lambda; \lambda$ is a wavelength) is the wave number of photoelectrons, R is the distance between the absorbing atoms and the scattering atoms, $2\delta_j$ the phase change in the electron waves entering and leaving the absorbing atoms, $|f_j(\pi)|$ is the amplitude of backscattering due to the j-th atom, $\exp(-\gamma R_j)$ is a correction term for correcting for the attenuation of electron waves, $\exp(-2k^2\sigma_j^2)$ is a correction term depending on the fluctuation σ_j of the positions of the scattering atoms relative to the absorbing atoms, N_j is the number of atoms existing within the range of R , from the atoms absorbing x-rays, and Ψ_j is the phase shift of waves due to the scattering atoms.

Multiplying both sides of equation (4) with $k |f_j(\pi)|^{-1}$ to express equation (4) in r space and taking the Fourier transform result in

$$\tilde{X}(r) = \frac{1}{2} \sum_i \frac{N_i}{\sigma_j R_j^2} \exp(-\gamma R_j) \exp\left(-\frac{(r - R_j)^2}{2\sigma_j^2}\right) \div \Delta(r) \quad (5)$$

This quantity has a peak at the position R_j of the j atoms around the absorbing atoms. That is, the radial distribution is found. In the above equation, $\Delta(r)$ indicates the error.

The accompanying figure is a graph showing the radial distribution function of a commercially available M_oS_2 reagent around M_o contained in J. The function was found according to the above equation. The distance R (in Å) from the M_o atom is plotted on the horizontal axis, while the intensity h of the absorption is plotted against the vertical axis. The coordination number M can be calculated from the positions (R) of the drawn peaks and the intensities (h). Thus,

$$M = h \times (R + \Delta R)^2 \ell B$$

where ΔR is the difference between each peak position and a reference peak position, and B is a correction value obtained by measurement of a reference substance.

Examination of the crystalline structure of M_oS_2 reveals that the coordination number of M_o -S and M_o - M_o is 6. Using M_oS_2 as a reference sample, the behavior of M_o which is contained in the novel catalyst and a metal belonging to the Group VI can be known.

EXAMPLE

50 Manufacture of Catalysts

Catalyst A:

First, 80 ml of impregnant was prepared from 29.0 g of molybdenum trioxide, 10.5 g of nickel carbonate (containing 43.3% by weight of nickel), 16.5 g of 85% phosphoric acid, and water. Then, 100 g of a carrier moulded out of γ -alumina was impregnated with the impregnant. The specific surface of the carrier was 280 m^2/g , and the pore volume was 0.75 ml/g. The impregnated carrier was dried at 100°C for 16 hours. Thereafter, it

was baked at 500°C for 2 hours to give rise to a catalyst consisting of 20% by weight of M_2O_3 , 4% by weight of NiO , 7% by weight of P_2O_5 , and alumina. Then, 20 g of this catalyst was impregnated with all of 10 ml of water solution of thioglycolic acid ($HSCH_2COOH$). The solution contained 7.5 g of thioglycolic acid. Thereafter, the catalyst was dried at 100°C for 16 hours to produce catalyst A.

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Catalyst B:

First, 100 g of a carrier of γ -alumina was prepared in the same way as in the above process and impregnated with impregnant of the same constitution as the aforementioned impregnant. The carrier was dried at 100°C for 16 hours. The dried carrier was impregnated with all of 10 ml of water solution of thioglycolic acid. The solution contained 7.5 g of thioglycolic acid. Then, the impregnated carrier was dried at 100°C for 16 hours to obtain catalyst B.

10 Catalyst C: A reaction tube made of stainless steel and having a fixed bed was prepared , and 3 m ℓ of catalyst B was loaded into the tube. Then, the catalyst was activated under the conditions:

amount of catalyst:	3 m ℓ
pressure:	atmospheric pressure
flow rate of hydrogen:	48 N ℓ /hr
time:	3 hours
temperature:	200°C

20 Evaluation of Activity

25 Using the aforementioned catalysts A, B, and C, Kuwait light oil of normal pressure was hydrotreated and desulfurized. The characteristics of the used light oil of normal pressure were as follows:

30 specific gravity (15/4°C):	0.848
sulfur:	1.61% by weight
nitrogen:	157 ppm by weight
35 distillation property (initial boiling point):	211°C
distillation property (50 vol% point):	340°C
distillation property (end point):	406°C

40 For the reaction, a reactor through which fluid flowed was employed. The conditions were as follows:

45 amount of catalyst:	3 m Ω
liquid space velocity of feedstock oil:	2.0 hr ⁻¹
reaction pressure (hydrogen pressure):	30 Kg/cm ²
50 reaction temperature:	330°C
ratio of hydrogen to oil:	300 N Ω / Ω
time for which oil is passed:	8 hours

55 The processed oil was sampled after 4 hours, after 6 hours, and after 8 hours. The amount of sulfur contained was measured, and the desulfurization ratio was calculated. The results are listed in Table 1.

Table 1

5 catalyst	coordination number of S	coordination number of M _o	desulfurization ratio (%)	remark
10 A (before) (after)	0.84 3.98	2.08	89.6	comparative example
15 B (before) (after)	0.70 3.55	0.00 1.98	95.9	example of invention
20 C (before) (after)	1.45 3.82	0.16 1.86	95.0	example of invention

Investigation of EXAFS

30 EXAFS of the catalyst A, B, C not used for activity evaluation and of the catalysts used for 360 hours was investigated by the EXAFS experimental facility of the High Energy Physics Laboratory, Japan. The measured absorption coefficients were subjected to Fourier transformation to find the radial distribution function around M_o. Also, the average coordination numbers of M_o-S and M_o-M_o were found. The coordination number of S around M_o, the coordination number of M_o around M_o, and activity are listed in Table 1.

35 It can be seen from Table 1 that the desulfurization ratio of the catalyst A is somewhat low, because it contains a sulfurizing agent after an active metal is once oxidized, and that the disulfurization ratios of the catalysts are quite high, because water-soluble compounds of active metals are contained in the pores together with sulfurizing agents.

40 The present invention offers a catalyst which hydrotreats highly active hydrocarbons without the need to presulfide them in a reactor.

Claims

- 45 1. A catalyst for hydrotreating hydrocarbons, the catalyst comprising a carrier of an inorganic oxide, the carrier containing a sulfurizing agent and a water-soluble compound of two metals one of which belongs to the Group VI of the Periodic Table, the other belonging to the Group VIII, the carrier having pores in which a precursor of a sulfide is formed, the coordination number of the closest Group VI metal that is found from the radial distribution function around the Group VI metal calculated by Fourier transform of the extended x-ray absorption fine structure of the precursor being less than 0.25 before use.
2. A catalyst according to claim 1, wherein the water-soluble compound further includes phosphorus.
3. A catalyst according to claim 2, wherein the phosphorus takes the form of P₂O₅ and accounts for 8% by weight, at most, of the water-soluble compound.
- 50 4. A catalyst according to claim 1, wherein the metal belonging to the Group VI of the Periodic Table is at least one of M_o and W, and wherein the metal belonging to the Group VIII is at least one of C_o and N_i.
- 55 5. A catalyst according to claim 1, wherein the sulfurizing agent is at least one compound selected from the group consisting of mercaptocarboxylic acid, its salts, bivalent mercaptan, amino-replaced mercaptan, thio-

acid, and mercaptocarboxylic esters given by the general formula HS-(CH₂)₂-COOR.

6. A catalyst according to claim 1, wherein the amount of the contained sulfurizing agent is one to three times the amount of sulfur in equivalent weight, the sulfur being necessary to form a highly active sulfide when the water-soluble compound is hydrotreated.

5 7. A catalyst according to claim 1, wherein the carrier of an inorganic oxide consists of alumina, silica alumina, or titania.

8. A catalyst according to claim 2, wherein the metal belonging to the Group VI of the Periodic Table is at least one of Mo and W, and wherein the metal belonging to the Group VIII is at least one of Co and Ni.

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Patentansprüche

1. Katalysator zur Wasserstoffbehandlung von Kohlenwasserstoffen, wobei der Katalysator einen Träger eines anorganischen Oxids enthält, wobei der Träger ein Schwefelungsmittel und eine wasserlösliche Verbindung aus zwei Metallen aufweist, von denen eines zur Gruppe VI und das andere zur Gruppe VIII des Periodensystems gehört, wobei der Träger Poren aufweist, in denen ein Vorläufer eines Sulfids gebildet wird, wobei die Koordinationszahl des am nächsten liegenden Metall der Gruppe VI, die durch die radiale Verteilungsfunktion um das Metall aus der Gruppe VI herum gefunden wurde, die durch Fourier-Transformation der erweiterten Röntgenstrahlabsorptionsfeinstruktur des Vorläufers berechnet wurde, vor der Verwendung weniger als 0,25 ist.

2. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß die wasserlösliche Verbindung weiterhin Phosphor enthält.

3. Katalysator nach Anspruch 2, dadurch gekennzeichnet, daß der Phosphor die Form von P₂O₅ annimmt und höchstens 8 Gewichtsprozent der wasserlöslichen Verbindung ausmacht.

25 4. Katalysator nach Anspruch 1 dadurch gekennzeichnet, daß das zur Gruppe IV des Periodensystems gehörende Metall wenigstens eines von Mo und W ist, und daß das zur Gruppe VIII gehörende Metall wenigstens eines von Co und Ni ist.

5 5. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß das Schwefelungsmittel wenigstens eine Verbindung aus der Gruppe, bestehend aus Merkaptokarbonsäure, deren Salzen, zweiseitigem Merkaptan, amino-ersetzen Merkaptan, Thiosäure, und Merkaptokarbonsäureestern nach der allgemeinen Formel HS-(CH₂)₂-COOR ist.

30 6. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß der enthaltene Gehalt von Schwefelungsmittels das Eins- bis Dreifache des Schwefelgehalts bezogen auf das äquivalente Gewicht ist, wobei der Schwefel erforderlich ist, um ein hoch-aktives Sulfid zu bilden, wenn die wasserlösliche Verbindung wasserstoffbehandelt wird.

35 7. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß der Träger eines anorganischen Oxids aus Aluminiumoxid, Siliziumoxid-Aluminiumoxid oder Titandioxid besteht.

8. Katalysator nach Anspruch 2, dadurch gekennzeichnet, daß das zur Gruppe VI des Periodensystems gehörende Metall wenigstens eines von Mo und W ist, und daß das zur Gruppe VIII gehörende Metall wenigstens eines von Co und Ni ist.

Revendications

45 1. Catalyseur pour l'hydrotraiteme nt des hydrocarbures, le catalyseur comprenant un matériau porteur constitué d'un oxyde inorganique, le matériau porteur contenant un agent sulfurisant et un composé soluble dans l'eau de deux métaux dont un appartient au groupe VI du Tableau Périodique des Éléments, l'autre appartenant au groupe VIII, le matériau porteur présentant des pores dans lesquels est formé un précurseur d'un sulfure, l'indice de coordination du métal le plus proche du Groupe VI qui est trouvé à partir de la fonction de distribution radiale autour du métal du Groupe VI calculé par la transformée de Fourier de la structure EXAFS du précurseur étant inférieur à 0,25 avant utilisation,

2. Catalyseur selon la revendication 1, caractérisé en ce que le composé soluble dans l'eau comprend en outre du phosphore.

3. Catalyseur selon la revendication 2, caractérisé en ce que le phosphore prend la forme de P₂O₅ et représente 8% en poids, au plus, du composé soluble dans l'eau.

55 4. Catalyseur selon la revendication 1, caractérisé en ce que le métal appartenant au Groupe VI du Tableau Périodique des Éléments est au moins un élément parmi le Mo et le W, et en ce que le métal appartenant au Groupe VIII est au moins un élément parmi le Co et le Ni.

5. Catalyseur selon la revendication 1, caractérisé en ce que l'agent de sulfurisation est au moins un composé sélectionné dans le groupe se composant d'acide mercaptocarboxylique, de ses sels, de mercaptan bivalent, de mercaptan substitué par des groupes aminés, de thioacide, et d'esters mercaptocarboxyliques donnés par la formule générale HS-(CH₂)₂-COOR.
- 5 6. Catalyseur selon la revendication 1, caractérisé en ce que la quantité d'agent sulfurisant contenu est égale à une quantité représentant une à trois fois la quantité de soufre en poids équivalent, le soufre étant nécessaire pour former un sulfure fortement actif lors de l'hydrotraitement du composé soluble à l'eau,
7. Catalyseur selon la revendication 1, caractérisé en ce que le matériau porteur constitué d'un oxyde inorganique se compose d'alumine, d'oxyde d'aluminium et silicium, ou de dioxyde de titane.
- 10 8. Catalyseur selon la revendication 2, caractérisé en ce que le métal appartenant au groupe VI du Tableau Périodique des Elements est au moins un élément parmi le Mo et le W, et en ce que le métal appartenant au Groupe VIII est au moins un élément parmi le Co et le Ni.

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